SCIENCE FOR CERAMIC PRODUCTION

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CERAMIC MEMBRANES WITH SELECTIVE LAYERS BASED ON SiO_2, TiO_2, AND ZrO_2

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A technology for producing ultrafiltration ceramic membranes using the sol-gel method has been developed. Experimental lots of membranes with selective layers based on SiO_2, TiO_2, and ZrO_2 are obtained, and their characteristics are investigated.

Ceramic membranes as a class of inorganic membranes are gaining popularity because of a number of their properties which give them an advantage over polymer membranes [1]. Selective layers in these membranes are mostly formed by the sol-gel method (RF Patent No. 2088313) [2 – 4]: a layer of the initial mixture is deposited on the surface of a flat or tubular support and subjected to drying and calcination. The main component of the initial mixture is a highly disperse metal oxide (in particular, metal oxide sols are used to obtain ultrafiltration selective layers). The most frequently used are oxides of aluminum, silicon, zirconium, titanium etc. The main properties of membranes, such as permeability, selectivity, etc. are determined by a number of factors, the most significant of which are the composition of the mixture used, the size of highly dispersed oxide particles, and the drying and calcination conditions.

The present paper shows the results obtained in the synthesis of selective ultrafiltration layers based on SiO_2, ZrO_2, and TiO_2 using the sol-gel method.

The initial high-dispersion metal oxides were SiO_2, ZrO_2, and TiO_2 hydrosols. The SiO_2 sol with an oxide content of about 32 wt.% consisted of particles with a mean size of 15 nm (the particle sizes were determined by the self-correlating function method using dynamic light dissipation). The ZrO_2 sol was obtained by hydrolysis of zirconyl chloride with its subsequent peptization in the presence of nitric acid and concentrating through ultrafiltration to about 25 wt.%. This sol contained x-ray-amorphous particles with a mean size of 42 nm. The TiO_2 sol was obtained in the same way, but the initial agent was titanium tetraethoxide. Two samples with about 30% sol content were obtained. The samples consisted of crystalline particles (a mixture of anatase with rutile) with mean diameters of 20 and 32 nm, respectively.

In order to obtain selective layers based on these sols, mixtures were prepared that contained, along with one of the specified sols, a water-soluble polymer (polyvinyl alcohol (PVA) or oxypropyl cellulose (OPC)) and glycerin as the plastifying agent. The selective layers were obtained with and without a substrate. The substrates were tubular microfiltration membranes (the inner and outer diameters of the tubes were 5 and 9.5 mm, respectively) with a mean pore radius of around 0.1 μm. The support (porosity 41%) and the selective layer of the microfiltration membrane were made on the basis of Al_2O_3.

Selective layers were deposited on the inner surface of the substrates with subsequent drying (for 24 h at room temperature) and calcination (the rate of the temperature rise did not exceed 60 K/h).

The size of the pores and the porosity of selective layers were identified by the mercury porometry method. The membranes on a substrate were tested as well for permeability with respect to distilled water and selectivity with respect to a polymer solution (polyvinyl pyrrolidone with molar weight 10,000 – 100,000 kg/kmole) and SiO_2 sols in tangential filtration.

The membranes based on Zr_2O sol without a substrate were obtained from a mixture containing 5% PVA and 1% glycerin, with a variable content of ZrO_2. The final calcination temperature was 700°C; the exposure 2 h. Some characteristics of the membranes are given in Table 1, and Fig. 1*b* shows the radius distribution of the pore volume in membrane 2. It can be seen that as the composition of the mixture

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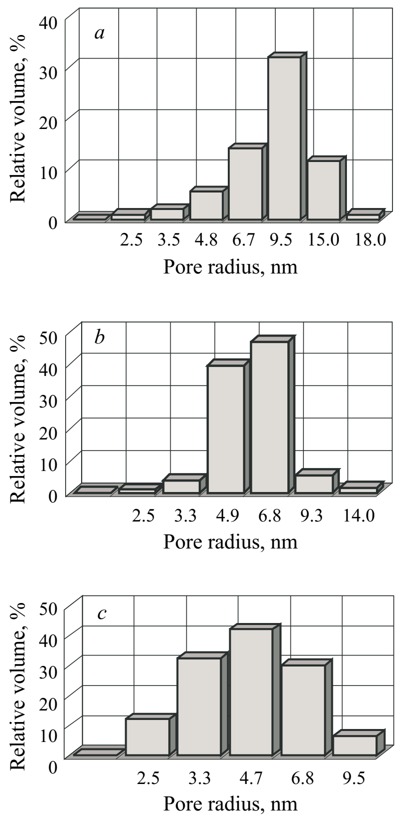

Fig. 1. Radius distribution of pore volume in membranes 2 (*a*), 5 (*b*), and 7 (*c*).

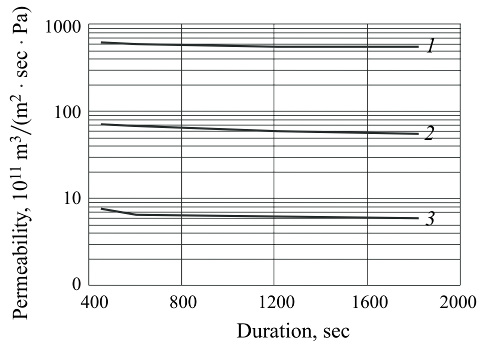

Fig. 2. Permeability with respect to distilled water in one-layer (*1*), two-layer (*2*), and three-layer (*3*) membranes based on ZrO_2 sol under a pressure difference of 3×10^5 Pa.

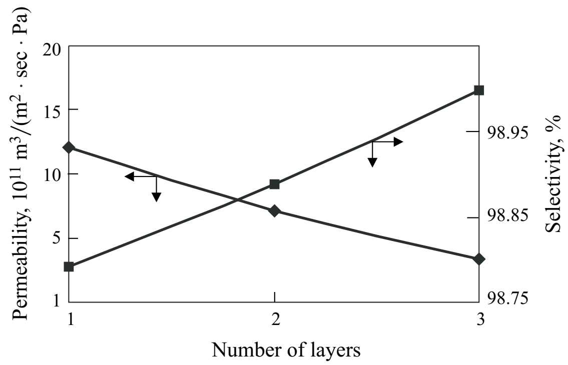

Fig. 3. The effect of the number of selective layers in ZrO_2-based membrane on its permeability and selectivity in concentrating SiO_2 sol (initial concentration of sol 0.01 g/liter, particle size 15 nm, pressure difference 3×10^5 Pa).

varies, the mean pore radius varies to some extent, with a sufficiently narrow distribution.

The same parameters of the TiO_2-based membranes without a substrate are shown in Table 2 and in Fig. 1*b* (in addition to sol, the mixture contained 3% OPC and 1% glycerin). The final calcination temperature of these membranes was 550°C.

The membranes based on TiO_2 have a higher porosity and greater specific surface area with a more narrow pore distribution by radius. It should be noted that these results were obtained in using sol with particles of size 32 nm. In using sol with a particle size of 20 nm, the results were similar, but the mean size of the membrane pores decreased proportionally to the size of the sol particles.

Figure 1*c* shows the radius distribution of pores in membrane 7 (without a substrate) based on SiO_2 sol (the initial mixture contained 25% SiO_2, 2% PVA, and 1% glycerin; the membrane was heat-treated at 600°C for 3 h).

Experimental lots of ultra- and nanofiltration membranes on substrates were produced on the basis of SiO_2, TiO_2, and ZrO_2. The test results for ZrO_2-based membranes with one, two, and three layers of consecutively deposited, dried, and fired film are shown in Figs. 2 – 4. It can be seen that the obtained membranes have high permeability and selectivity levels. Thus, the selectivity of the ultrafiltration membranes based on ZrO_2 in the course of concentration of SiO_2 sol (particle size 15 nm) varied from 98.8 to 99.0% (Fig. 3), while preserving sufficiently good permeability. High selec-

TABLE 1

Parameter	Membrane		
	1	2	3
ZrO_2 content in the mixture, %	5	9	12
Average pore radius, nm	3.0	9.0	5.0
Porosity, %	33.0	45.8	41.3
Specific surface area, m^2/g	17.4	25.3	26.5

TABLE 2

Parameter	Membrane		
	4	5	6
TiO_2 content in the mixture, %	5	9	12
Average pore radius, nm	7.0	7.0	5.0
Porosity, %	67.2	56.0	50.1
Specific surface area, m^2/g	125.9	104.5	92.1

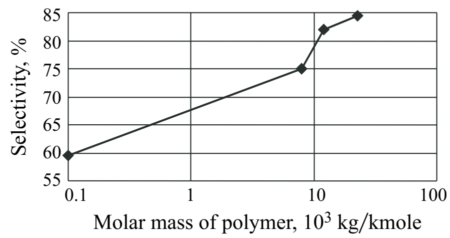

Fig. 4. Dependence of selectivity in a three-layer ultrafiltration ZrO_2-based membrane on the molar mass of polyvinyl pyrrolidone (initial concentration of sol 5 g/liter, pressure difference 3×10^5 Pa).

tivity values are exhibited as well in filtration of polyvinyl pyrrolidone solutions (Fig. 4), in which case the membrane stops even monomers with a molar mass of 111 kg/kmole.

Thus, the obtained membranes in their main parameters, i.e., permeability and selectivity, are comparable to the TECHSEP utrafiltration membranes, whose capacity with respect to distilled water ranges from 2×10^{-10} to 3×10^{-10} $m^3/(m^2 \cdot sec \cdot Pa)$.

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